EUR 803.e
REPRINT

EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

SURFACE TENSION OF LIQUID NITRATE SYSTEMS

by

G. BERTOZZI and G. STERNHEIM

1965

Joint Nuclear Research Center
Ispra Establishment - Italy
Chemistry Department
High Temperature Chemistry Service

Reprinted from
THE JOURNAL OF PHYSICAL CHEMISTRY
Vol. 68, No. 10 - 1964

EUR 803.e
REPRINT

SURFACE TENSION OF LIQUID NITRATE SYSTEMS by G. BERTOZZI and G. STERNHEIM

European Atomic Energy Community - EURATOM
Joint Nuclear Research Center
Ispra Establishment - Italy
Chemistry Department
High Temperature Chemistry Service
Reprinted from ,,The Journal of Physical Chemistry"
Vol. 68, No. 10 - 1964, pp. 2908-2912

Surface tension measurements are reported for eight binary alkali nitrate systems and for five silver nitrate-alkali nitrate systems, in the temperature range from the melting point to about 400°. A linear dependence on temperature always holds. With regard to the alkali nitrate systems, it is found that the surface tension of the mixtures is well represented by the semiempirical expression : $j = x_1 j_1 + x_2 j_2 - 1900 x_1 x_2 [(d_1 - d_2)/(d_1 + d_2)]^2$, where j_1 and j_2

EUR 803.e
REPRINT

SURFACE TENSION OF LIQUID NITRATE SYSTEMS by G. BERTOZZI and G. STERNHEIM

European Atomic Energy Community - EURATOM
Joint Nuclear Research Center
Ispra Establishment - Italy
Chemistry Department
High Temperature Chemistry Service
Reprinted from ,,The Journal of Physical Chemistry"
Vol. 68, No. 10 - 1964, pp. 2908-2912

Surface tension measurements are reported for eight binary alkali nitrate systems and for five silver nitrate-alkali nitrate systems, in the temperature range from the melting point to about 400°. A linear dependence on temperature always holds. With regard to the alkali nitrate systems, it is found that the surface tension of the mixtures is well represented by the semiempirical expression : $j = x_1 j_1 + x_2 j_2 - 1900 x_1 x_2 [(d_1 - d_2)/(d_1 + d_2)]^2$, where j_1 and j_2

EUR 803.e
REPRINT

SURFACE TENSION OF LIQUID NITRATE SYSTEMS by G. BERTOZZI and G. STERNHEIM

European Atomic Energy Community - EURATOM
Joint Nuclear Research Center
Ispra Establishment - Italy
Chemistry Department
High Temperature Chemistry Service
Reprinted from ,,The Journal of Physical Chemistry"
Vol. 68, No. 10 - 1964, pp. 2908-2912

Surface tension measurements are reported for eight binary alkali nitrate systems and for five silver nitrate-alkali nitrate systems, in the temperature range from the melting point to about 400°. A linear dependence on temperature always holds. With regard to the alkali nitrate systems, it is found that the surface tension of the mixtures is well represented by the semiempirical expression : $j = x_1 j_1 + x/j_2 - 1900 x_1 x_2 [(d_1 - d_2)/(d_1 + d_2)]^2$, where j_1 and j_2

are the surface tensions of the two pure components and x_1 and x_2 are their mole fractions; d_1 and d_2 are the interionic distances of the pure salts. Mixtures of silver nitrate with the alkali nitrates as the second component exhibit surface tension isotherms which become more convex toward the abscissa as the radius of the alkali metal cation increases; the deviations from linearity of the surface specific enthalpy as a function of the composition are found to increase with the size of the alkali metal. This trend is interpreted as an increasing interaction of covalent character.

are the surface tensions of the two pure components and x_1 and x_2 are their mole fractions; d_1 and d_2 are the interionic distances of the pure salts. Mixtures of silver nitrate with the alkali nitrates as the second component exhibit surface tension isotherms which become more convex toward the abscissa as the radius of the alkali metal cation increases; the deviations from linearity of the surface specific enthalpy as a function of the composition are found to increase with the size of the alkali metal. This trend is interpreted as an increasing interaction of covalent character.

are the surface tensions of the two pure components and x_1 and x_2 are their mole fractions; d_1 and d_2 are the interionic distances of the pure salts. Mixtures of silver nitrate with the alkali nitrates as the second component exhibit surface tension isotherms which become more convex toward the abscissa as the radius of the alkali metal cation increases; the deviations from linearity of the surface specific enthalpy as a function of the composition are found to increase with the size of the alkali metal. This trend is interpreted as an increasing interaction of covalent character.

[Reprinted from the Journal of Physical Chemistry, 68, 2908 (1964).]

Surface Tension of Liquid Nitrate Systems

by G. Bertozzi and G. Sternheim

Chemistry Department, High Temperature Chemistry, Euratom, Ispra, Italy *(Received April 13, 1964)*

Surface tension measurements are reported for eight binary alkali nitrate systems and for five silver nitrate–alkali nitrate systems, in the temperature range from the melting point to about 400°. A linear dependence on temperature always holds. With regard to the alkali nitrate systems, it is found that the surface tension of the mixtures is well represented by the semiempirical expression: $j = x_1j_1 + x_2j_2 - 1900x_1x_2[(d_1 - d_2)/(d_1 + d_2)]^2$, where j_1 and j_2 are the surface tensions of the two pure components and x_1 and x_2 are their mole fractions; d_1 and d_2 are the interionic distances of the pure salts. Mixtures of silver nitrate with the alkali nitrates as the second component exhibit surface tension isotherms which become more convex toward the abscissa as the radius of the alkali metal cation increases; the deviations from linearity of the surface specific enthalpy as a function of the composition are found to increase with the size of the alkali metal. This trend is interpreted as an increasing interaction of covalent character.

Introduction

Binary systems of molten nitrates were recently investigated by Kleppa and co-workers, who measured the heats of mixing of all the alkali nitrate binary systems[1,2] and of four silver nitrate-alkali nitrate systems.[3]

All the alkali nitrate mixtures are exothermic, and the thermal effect increases with the difference in size of the two alkali ions. Silver nitrate mixtures containing lithium or sodium nitrate were found to be endothermic, whereas those with potassium or rubidium nitrate were found to be exothermic.

We measured the surface tension of the same systems and tried to relate the results to the sizes of the ions in the mixture. Formerly, Boardman, Palmer, and Heymann[4] and Dahl and Duke[5] carried out measurements on the surface tension of sodium–potassium nitrate mixtures; silver–sodium and silver–potassium nitrate mixtures were investigated by Dahl and Duke[5] and by Bloom, Davis, and James.[6] All of these authors compared their experimental results with the values predicted by Guggenheim's equation for ideal mixtures.[7]

Experimental

The Wilhelmy slide method[8-10] was used; it consists of measuring the maximum pulling force necessary to detach a thin platinum plate from the liquid surface. For a straight edge, the force is proportional to the sur-

(1) O. J. Kleppa, *J. Phys. Chem.*, **64**, 1937 (1960).

(2) O. J. Kleppa and L. S. Hersh, *J. Chem. Phys.*, **34**, 351 (1961)

(3) O. J. Kleppa, R. B. Clarke, and L. S. Hersh, *ibid.*, **35**, 175 (1961).

(4) N. K. Boardman, A. R. Palmer, and E. Heymann, *Trans. Faraday Soc.*, **51**, 277 (1955).

(5) J. L. Dahl and F. R. Duke, U. S. Atomic Energy Commission Report ISC-923 (1958).

(6) H. Bloom, F. G. Davis, and D. W. James, *Trans. Faraday Soc.*, **56**, 1179 (1960).

(7) E. A. Guggenheim, "Mixtures," Oxford University Press, London, 1952.

face tension of the liquid. The force is measured as the maximum increase of the apparent weight of the plate, according to the formula, $\Delta W_{max} = 2aj$, where a is the length of the edge, W is the weight increase in dynes, and j is the surface tension in dynes/cm.

The platinum plate was 15 mm. in edge length and 0.1 mm. thick. A Mettler recording balance was used for weight measurements. The temperature was measured a few millimeters above the surface of the melt and was accurate to ±1°.

Merck and B.D.H. salts of analytical purity were carefully dried and used without further purification. Results were reproducible within 0.5% in the whole temperature range, from the melting point up to ~400°; measurements at higher temperature were not performed because of the thermal decomposition of silver and lithium salts.

Results

The surface tensions of the following binary systems were measured: (K–Li)NO_3, (K–Na)NO_3, (K–Rb)NO_3, (K–Cs)NO_3, (Li–Rb)NO_3, (Li–Cs)NO_3, (Na–Rb)NO_3, (Na–Cs)NO_3, (Li–Ag)NO_3, (Na–Ag)NO_3, (K–Ag)NO_3, (Rb–Ag)NO_3, and (Cs–Ag)NO_3. Besides the pure components, we selected the 25, 50, and 75% M mixtures of each system for the measurements. The surface tension of all the systems always shows a linear dependence on temperature, the temperature coefficient being of the order of 0.07 dyne/cm. deg. The surface tension equations for all of the mixtures are given in Table I.

The surface tension isotherms at 350° are plotted in Fig. 1–4.[11] The systems (K–Na)NO_3, (K–Rb)NO_3, (K–Cs)NO_3, and (Li–Ag)NO_3 exhibit nearly linear isotherms, whereas the isotherms of the other systems are more pronouncedly convex.

Discussion

It is well known that the surface tension of "ideal" systems is not a linear function of the composition. Guggenheim's treatment leads to the equation

$$\exp(-ja/kT) = x_1 \exp(-j_1 a/kT) + x_2 \exp(-j_2 a/kT)$$

This treatment, which was successfully applied to many systems, requires that the molecular surface areas of the components are equal; in our case this condition is not fulfilled for the major part of the systems; for instance, the surface area for lithium nitrate is 16.3 × 10^{-16} cm.²/molecule, whereas for cesium nitrate it is 23.2 × 10^{-16} cm.²/molecule. In addition to this, it was shown by Blander[12] that ionic mixtures with cationic radii different from each other in any case cannot be regarded as ideal. Guggenheim extended his treatment

Table I

KNO_3, mole %	$KNO_3 + LiNO_3$
100	$j = 139.8 - 0.081t$
75	$j = 133.6 - 0.070t$
50	$j = 129.6 - 0.062t$
25	$j = 127.9 - 0.056t$
0	$j = 129.9 - 0.055t$

KNO_3, mole %	$KNO_3 + NaNO_3$
75	$j = 138.5 - 0.076t$
50	$j = 139.7 - 0.076t$
25	$j = 139.8 - 0.072t$
0	$j = 137.6 - 0.060t$

KNO_3, mole %	$KNO_3 + RbNO_3$
75	$j = 138.5 - 0.083t$
50	$j = 136.9 - 0.083t$
25	$j = 135.0 - 0.082t$
0	$j = 134.3 - 0.083t$

KNO_3, mole %	$KNO_3 + CsNO_3$
75	$j = 133.7 - 0.079t$
50	$j = 129.4 - 0.077t$
25	$j = 125.1 - 0.074t$
0	$j = 122.1 - 0.074t$

$NaNO_3$, mole %	$NaNO_3 + RbNO_3$
75	$j = 135.4 - 0.068t$
50	$j = 133.7 - 0.073t$
25	$j = 132.5 - 0.076t$

$NaNO_3$, mole %	$NaNO_3 + CsNO_3$
75	$j = 130.5 - 0.068t$
50	$j = 127.3 - 0.074t$
25	$j = 123.4 - 0.072t$

$LiNO_3$, mole %	$LiNO_3 + RbNO$
75	$j = 125.0 - 0.059t$
50	$j = 129.6 - 0.074t$
25	$j = 130.0 - 0.075t$

$LiNO_3$, mole %	$LiNO_3 + CsNO_3$
75	$j = 124.3 - 0.070t$
50	$j = 124.3 - 0.076t$
25	$j = 122.9 - 0.075t$

$AgNO_3$, mole %	$AgNO_3 + LiNO_3$
100	$j = 163.7 - 0.066t$
75	$j = 153.5 - 0.067t$
50	$j = 145.7 - 0.068t$
25	$j = 137.8 - 0.064t$

$AgNO_3$, mole %	$AgNO_3 + N_aNO_3$
90	$j = 159.2 - 0.066t$
75	$j = 153.0 - 0.065t$
50	$j = 146.7 - 0.066t$
25	$j = 141.6 - 0.065t$

$AgNO_3$, mole %	$AgNO_3 + KNO_3$
90	$j = 156.5 - 0.073t$
75	$j = 149.0 - 0.073t$
50	$j = 143.0 - 0.076t$
25	$j = 141.9 - 0.082t$

$AgNO_3$, mole %	$AgNO_3 + RbNO_3$
90	$j = 151.7 - 0.069t$
75	$j = 143.4 - 0.070t$
50	$j = 136.9 - 0.073t$
25	$j = 134.0 - 0.077t$

$AgNO_3$, mole %	$AgNO_3 + CsNO_3$
90	$j = 148.4 - 0.072t$
75	$j = 140.1 - 0.073t$
50	$j = 130.3 - 0.072t$
25	$j = 126.1 - 0.075t$

(8) L. Wilhelmy, *Ann. Physik*, **119**, 177 (1863).

(9) R. Ruissen, *Rec. trav. chim.*, **65**, 580 (1946).

(10) A. W. Adamson, "Physical Chemistry of Surfaces," Interscience Publishers, Inc., New York, N. Y., 1960.

(11) The surface tension of cesium nitrate at 350° was calculated by extrapolating below the melting point.

(12) M. Blander, *J. Chem. Phys.*, **34**, 697 (1961).

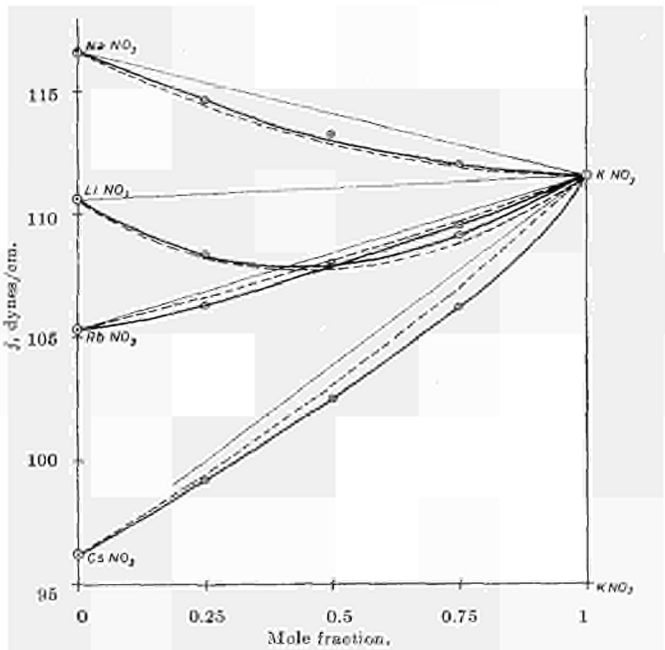


Figure 1. Surface tension isotherms at 350° for the systems $(K–Li)NO_3$, $(K–Na)NO_3$, $(K–Rb)NO_3$, and $(K–Cs)NO_3$: ⊙—⊙, experimental curve; - - - -, eq. 2; ———, linearity.

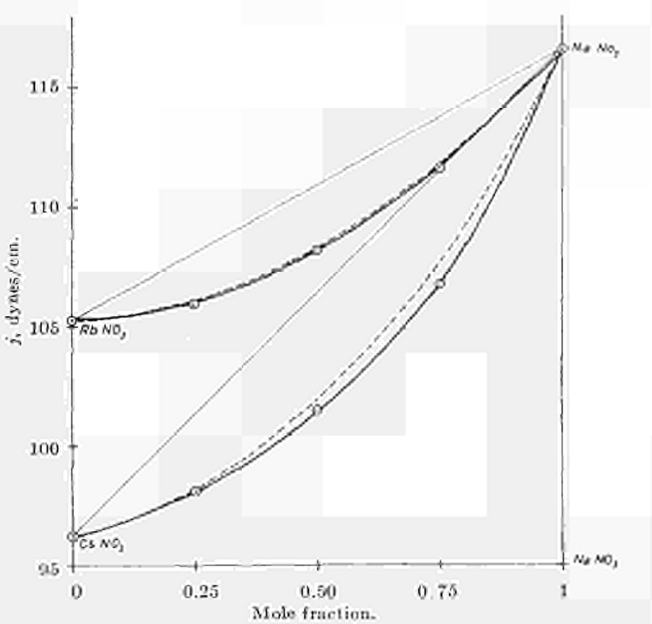


Figure 2. Surface tension isotherms at 350° for the systems $(Na–Rb)NO_3$ and $(Na–Cs)NO_3$: ⊙—⊙, experimental curve; - - - -, eq. 2; ———, linearity.

to regular mixtures, and an improved derivation was later developed by Hoar and Melford[13] which is consistent with the Gibbs relation.

As in our case, deviations are often remarkable and cannot be accounted for by Guggenheim's or Hoar's

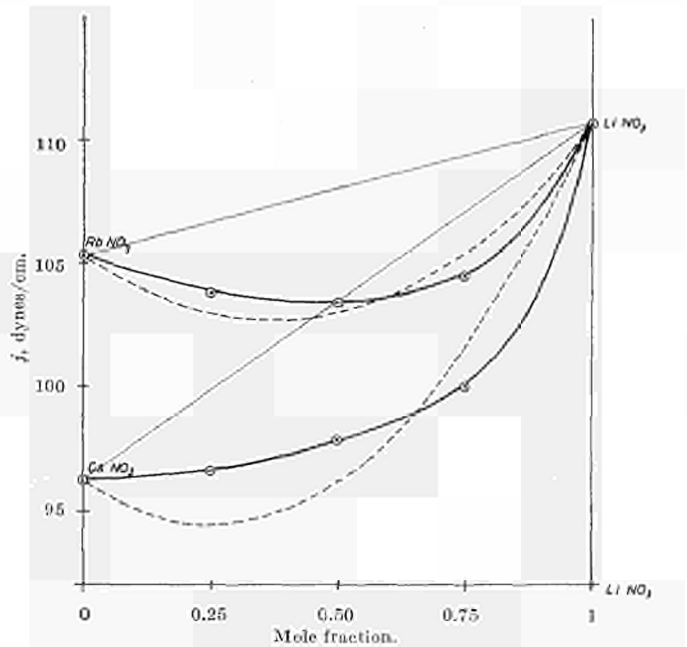


Figure 3. Surface tension isotherms at 350° for the systems $(Li–Rb)NO_3$ and $(Li–Cs)NO_3$: ⊙—⊙, experimental curve; - - - -, eq. 2; ———, linearity.

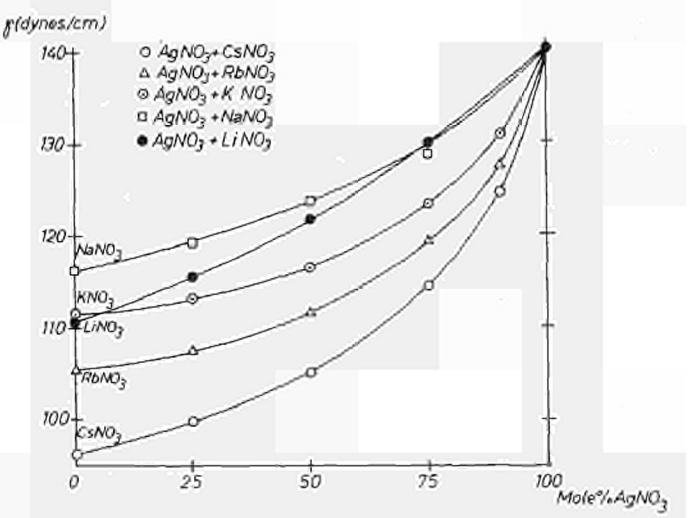


Figure 4. Surface tension isotherms at 350° for the systems $(Li–Ag)NO_3$, $(Na–Ag)NO_3$, $(K–Ag)NO_3$, $(Rb–Ag)NO_3$, and $(Cs–Ag)NO_3$.

equations for regular mixtures, even by allowing for large values of the interchange energy. We preferred to follow a suggestion by Blander[14] and tried to relate deviations from linearity to a semiempirical equation. Good agreement with the experimental results was found for the alkali nitrate systems.

(13) T. P. Hoar and D. A. Melford, *Trans. Faraday Soc.*, **53**, 315 (1957).

(14) M. Blander, private communication.

Alkali Nitrate Systems. In this case, deviations from linearity do not depend on the difference between the surface tension of the pure components but rather on the difference in size between the two alkali ions in the mixture.

In Fig. 5 we plotted the maximum values of the deviations of the surface tension isotherms from linearity for each system *vs.* the parameter $[(d_1 - d_2)/(d_1 + d_2)]^2$, where d_1 and d_2 are cation–anion center distances for salts 1 and 2, respectively, and were calculated as the sum of the radii of the cation and the anion (the Goldschmidt values were chosen).

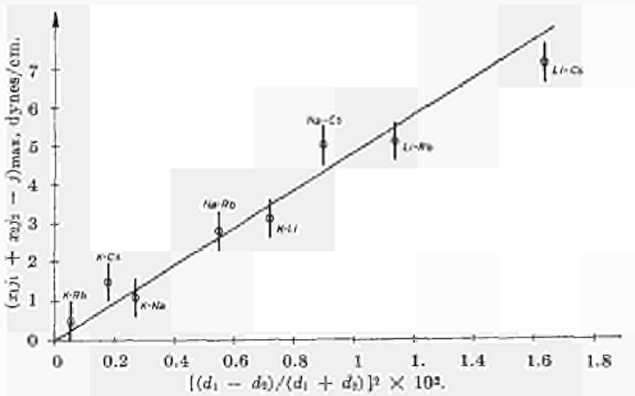


Figure 5. Maximum deviations of surface tension isotherms from linearity as a function of the parameter $[(d_1 - d_2)/(d_1 + d_2)]^2$.

A linear dependence holds

$$(x_1j_1 + x_2j_2 - j)_{max} = 475[(d_1 - d_2)/(d_1 + d_2)]^2$$

The choice of the parameter $[(d_1 - d_2)/(d_1 + d_2)]^2$ relies upon a calculation made by Forland[15] on the coulombic energy change on mixing in a linear array of ions, provided that the nearest and next nearest neighbors only are considered; the usefulness of this parameter was first tested by Kleppa and co-workers,[2] who found for the heats of mixing in liquid alkali nitrate systems the empirical expression

$$\Delta H = -x_1x_2U[(d_1 - d_2)/(d_1 + d_2)]^2 \quad \text{(cal./mole)}$$

Accordingly, we set up tentatively the semiempirical equation

$$\Delta j = x_1j_1 + x_2j_2 - j = Kx_1x_2[(d_1 - d_2)/(d_1 + d_2)]^2 \quad (1)$$

where x_1 and x_2 are the molar fractions of the components; the numerical value of K is 1900 for all the systems and was calculated by putting $Kx_1x_2 = 475$ when $x_1 = x_2 = 1/2$. Equation 1 can be rewritten as

$$j = x_1j_1 + x_2j_2 - Kx_1x_2[(d_1 - d_2)/(d_1 + d_2)]^2 \quad (2)$$

Thus we have an expression for the surface tension of the mixture as a function of the composition, of the surface tension of the components, and of the size of the two alkali ions. The isotherms calculated from this equation are reported as dotted lines in Fig. 1–3. The agreement is satisfactory except for the systems (Li–Rb)NO_3 and (Li–Cs)NO_3; the behavior of these two systems can be interpreted by considering that here the lithium ion, which has a high polarizing power, is mixed with the largest ions which are easily polarizable, so that big changes in polarization energy arise which cannot be predicted by eq. 2.

Silver Nitrate–Alkali Nitrate Systems. In this case, the shape of the surface tension isotherms is not a function of the difference between the size of the cations in the mixture, so that the parameter $[(d_1 - d_2)/(d_1 + d_2)]^2$ is useless here. On the contrary, it is apparent from Fig. 4 that the surface tension isotherms are more convex, the larger the radius of the alkali ion, *i.e.*, increasingly in the order, Li < Na < K < Rb < Cs, independent of the value of the surface tension of the components. This behavior is apparent by comparing the isotherms of (Li–Ag)NO_3 with that of (K–Ag)NO_3: they have nearly the same limiting values but are greatly different with regard to the shape.

Similar trends were observed by Dahl and Duke[5] for lead chloride–alkali metal chloride systems and were interpreted by the authors on the basis of covalent character of the bonds in the melt increasing with decreasing the polarizing power of the alkali ions.

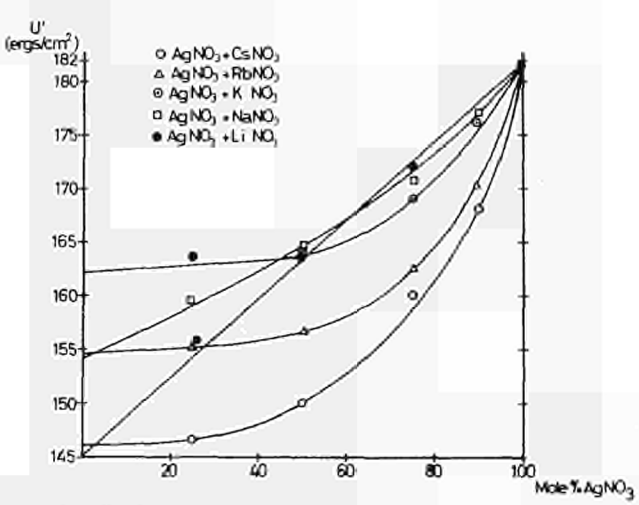


Figure 6. Surface specific enthalpy as a function of the composition.

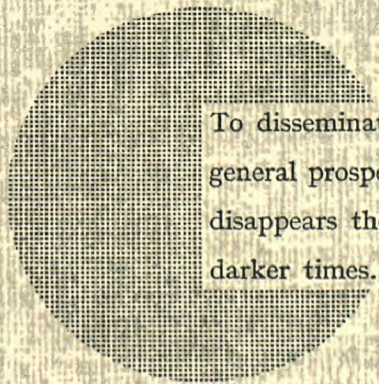
(15) T. Forland, *J. Phys. Chem.*, **59**, 152 (1955).

Since the specific surface enthalpy, $U' = j - T(dj/dT)$, is more informative than the surface tension with regard to the structural nature of the interface,[10] and Bloom, Davis, and James[6] stated that this quantity could provide information on the nature of the bonds in melts, we plotted (Fig. 6) the surface specific enthalpy as a function of the composition. It shows a linear dependence on composition in the case of (Li–Ag)NO_3; there is a slight negative deviation from linearity for (Na–Ag)NO_3, whereas large negative deviations are present in the remaining systems increasing with the radius of the alkali ion.

This behavior can be interpreted as an increasing interaction of covalent character, in agreement with Thurmond's observations concerning liquid mixtures of silver bromide with lithium and rubidium bromides.[16] The author pointed out that in pure liquid silver bromide there is a resonance between covalent and ionic bonds; if a small cation such as Li^+ or Na^+ is added, its strong electric field will weaken this resonance, whereas large cations with a weak field will enhance the covalent bonding. This point of view was extended by Kleppa and co-workers[3] to the corresponding nitrate systems.

Acknowledgments. The authors are indebted to Mr. G. Soldani for having performed some surface tension measurements. They wish furthermore to acknowledge the interesting discussion which they had with Milton Blander from North American Aviation Science Center, during his visit.

(16) C. D. Thurmond, *J. Am. Chem. Soc.*, **75**, 3928 (1953).



To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

CDNA00803ENC